3

BASIC ELEMENTS OF SPECTROSCOPY

Introduction

Spectroscopy is the study of interaction between matter and electromagnetic waves. Historically spectroscopy originated through the study of visible light dispersed according to its wavelength. e.g., by a prism. Later this concept was extended greatly to comprise any interaction with electromagnetic waves as a function of wavelength. Spectroscopic data is often represented by a spectrum. Spectrum is a plot of the response of interest as a function of wavelength.

Daily observations of colour can be related to spectroscopy. Neon light is a direct application of atomic spectroscopy. Neon and other noble gases have a characteristic emission colours. A commonly encountered molecular spectrum is that of NO_2. NO_2 has a characteristic red absorption colours.

Atoms and molecules have unique spectra. These spectra can be interpreted to derive information about the atoms and molecules and they can also be used to detect, identify and quantify chemicals.

The quantisation of energy

According to classical physics, radiation which behaves like an oscillator (radiation originates from an oscillating charge), should have continuous energy distribution. In 1900 Max Planck made a daring assumption that the oscillators of radiation should not have a continuous distribution of possible energies, but it must have specific energies.

According to Planck an oscillator emits radiation of energy $h\nu$ when it jumps from one energy state to the next lower state. When it jumps from lower state to the next higher state it absorbs radiation of energy $h\nu$. In other words emission and absorption take place not in continuous manner as predicted by classical physics but in discrete manner, each discrete bundle carries an energy $h\nu$, where h is called Planck's constant whose value is

$$h = 6.626 \times 10^{-34} \, Js$$

Each discrete bundle of energy is called as a quantum of energy. This idea of Planck later extended to cover many other forms of the energy of matter.

Here we deal with energy of molecules. A molecule may possess rotational en-

ergy, vibrational energy and electronic energy. Rotational energy is due to the rotation of molecules about its centre of gravity. Vibrational energy is due to the periodic displacement of molecule's atoms from their equilibrium positions. Since the electrons associated with atoms are in unceasing motion, we can say that molecules also possess electronic energy. The electrons occupy one of its discrete levels. These energy levels are quantised. i.e., when electrons jump from one level to another, they release or absorb finite amount of energy. This idea can be extended to molecules. A molecule can exist in a variety of rotational, vibrational energy levels. When it moves from one level to another energy involved is quantised like electronic energy. Let E_1 and E_2 be two rotational energy levels of a molecule. The molecule can go from level E_1 to E_2 by absorbing energy $E_2 - E_1$. According to Planck, this energy difference has the form
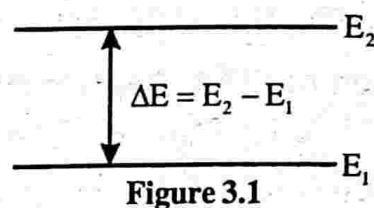
$$E_2 - E_1 = h\nu$$

where h is the Planck's constant and ν is the frequency of radiation absorbed. Similarly when the molecule jumps from level E_2 to E_1, the excess energy is released in the form of electromagnetic radiation with energy $h\nu$

i.e., $$E_2 - E_1 = h\nu$$

This extension of idea of Planck to molecules was confirmed experimentally.

Suppose a molecule is in level E_1 and is irradiated with a single frequency ν, then the energy $E_2 - E_1 = h\nu$ will be absorbed from the incident beam and the molecule will jump to energy level E_2. The radiation after interaction with the molecule is allowed to fall on a detector, will show that its intensity has decreased. If we use a beam containing several frequencies for irradiation, then the detector will show that energy has been absorbed only from that frequency $\nu = \dfrac{E_2 - E_1}{h}$ and all other frequencies undiminished in intensity. The spectrum so obtained is called an absorption spectrum.

If the molecule is in the energy level E_2 may jump to level E_1 by emitting radiation of energy $E_2 - E_1 = h\nu$. The detector would show that the radiation emitted has a frequency of $\nu = \dfrac{E_2 - E_1}{h}$. The spectrum so obtained is called an emission spectrum.

Figure 3.1

The energy differences between the rotational, vibrational and electronic energy levels are very small since $h = 6.626 \times 10^{-34}$ Js. The energy differences are measured in joules per molecule. To have an appreciable energy change we take a gram molecule of a substance. It contains 6.02×10^{23} molecules. To get the total energy change $h\upsilon$ has to be multiplied by 6.02×10^{23}.

Joule is not the only unit used to represent the transitions between energy states. Various other characteristics such as ν, λ of the absorbed or emitted radiation during transitions between energy states can also be used as units. Frequency ν is expressed in hertz, wavelength λ in metre and wave number in m^{-1}.

Regions of the spectrum

Spectroscopy is a sufficiently a broad field that many sub disciplines exist each with numerous implementations of specific spectroscopic techniques. Types of spectroscopy are distinguished by the type of radiative energy involved in the interaction. This type includes

1. Electromagnetic radiation. It was the first source of energy used for spectroscopic studies. Techniques that employ electromagnetic radiation are typically classified by the wavelength (frequency) region of the spectrum and include γ-ray, X-ray, u-v ray. Infrared, microwave, nuclear magnetic resonance (nmr) and electron spin resonance (e.s.r) spectroscopy.

2. Particles due to their de-broglic wavelength can also be a source of radiative energy. Both electrons and neutrons are commonly used.

3. Acoustic spectroscopy involves radiated pressure waves as the source of energy.

4. Mechanical methods can be employed to impart radiating energy similar to acoustic waves to solid materials.

Among the four types discussed above we are interested only in the first type.

Electromagnetic spectrum and the corresponding spectroscopy

The orderly distribution of electromagnetic radiations according to their wavelength or frequency is called electromagnetic spectrum. The range of the electromagnetic spectrum varies from 3×10^7 Hz to 3×10^{20} Hz (10m to 1 picometre). The whole electromagnetic spectrum has been classified into different regions in order of increasing frequency (decreasing wavelength) according to their type of excitation. The boundaries between the regions are not sharp. i.e., There is overlapping in certain regions of the spectrum. Each region of the spectrum is associated with different molecular processes. Accordingly we have six regions of spectrum.

1. Radio frequency region

This region extends from 3×10^7 Hz to 3×10^{10} Hz (10m to 1cm wavelength).

This frequency region is important to a spectroscopist in the sense that the phenomenon of nuclear magnetic resonance (n.m.r) and electron spin resonance (e.s.r) occur at this frequency region. The nuclear magnetic resonance occur at the lower part of the radio frequency region (≈ 100MHz) and electron spin resonance occur at the upper part of the radio frequency region ($\approx 10^{10}$ Hz). Since this frequency is considerably at the end of radio frequency region we can also say that e.s.r. occurs at the long wavelength edge of the microwave region.

Nuclear magnetic resonance (n.m.r)

If we consider a nucleus as a point charge spinning about its own axis, it constitutes a circular current which in turn produces a magnetic dipole. In other words the spinning particle behaves as a tiny bar magnet placed along the spin axis. When such nucleus is subjected to an external magnetic field, it is due to interaction between two fields the spin associated with the nucleus change direction. As a result of transition of nuclear spins between energy levels, emission or absorption spectra is obtained. This phenomenon is called nuclear magnetic resonance. This occurs at a frequency of about 100MHz. The energy change involved in the change of nuclear spin is of the order of 10^{-2} joules / mole.

We have
$$E = h\nu = 6.62 \times 10^{-34} \times 100 \times 10^6$$
$$= 6.62 \times 10^{-26} \text{ J}$$

For one mole $E = Nh\nu = 6.02 \times 10^{23} \times 6.62 \times 10^{-26}$
$$= 3.99 \times 10^{-2} \text{ joules / mole}$$

Electron spin resonance (e.s.r)

Electron is a charged particle spinning about an axis constitues a circular electric current which in turn produces a magnetic dipole. This dipole interacts with a magnetic field. As a result of interation a transition of electron spins between energy levels occur. This gives rise to emission or absorption spectrum. This phenomenon is called electron spin resonances. This occurs at a frequency about 10^{10} Hz. The energy change involved in the change of electron spin is of the order of 10 joules / mole.

$$E = h\nu = 6.62 \times 10^{-34} \times 10^{10} = 6.62 \times 10^{-24} \text{ J}$$

For 1 mole
$$E = Nh\nu = 6.02 \times 10^{23} \times 6.62 \times 10^{-24}$$
$$= 3.99 \text{ joule / mole.}$$

2. Microwave region

This region extends from 3×10^{10} Hz to 3×10^{12} Hz (1cm to 100μm wavelength).

For a spectroscopists the microwave region is concerned with the study of rotating molecules and is called as rotational spectroscopy. The energy change involved due to rotation of molecules is of the order of 100 joules / mole. (Remember $E = Nh\nu$).

We know that dielectrics are of two types namely non-polar and polar. Polar dielectrics like water, alcohol, CO_2, NH_3, HCl etc. are polar molecules. In polar molecules the centre of mass of positive charges does not coincide with centre of mass of negative charges. In this each molecule has zero dipole moment.

Now we consider the pure rotation of a polar molecule. Pure rotation means centre of gravity of the molecule doesnot move. During rotation the positive and negative charges change their places periodically (see figure below). This is similar to a fluctuating electric field of radiation.
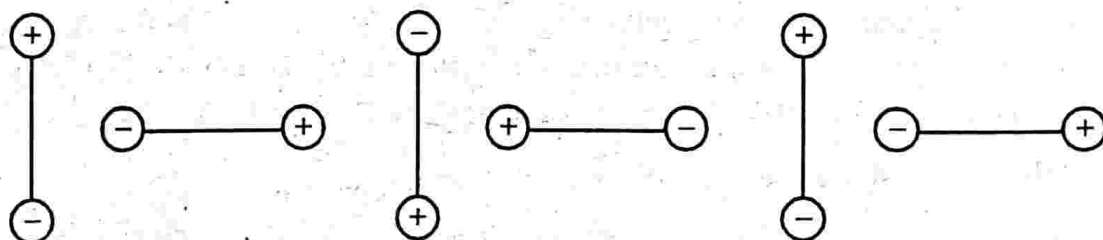

Figure 3.2

Here fluctuation of dipole moment takes place. Regular fluctuation of dipole moment results in interaction in which energy can be absorbed or emitted. This gives rise to a spectrum called rotation spectrum. The frequency of the spectrum corresponds to microwave region. Thus all molecules having a permanent dipole moment are said to be microwave active. On the other hand non polar molecules which do not have permanent dipole moment no interaction takes place and no spectrum. Thus non polar molecules are said to be microwave inactive.

3. Infrared region

This region extends from 3×10^{12} Hz to 3×10^{14} Hz (100μm to 1μm wavelength).

The spectrum arises due to vibrational motion of a molecule is called vibration spectrum. The study of vibration spectrum is called vibrational spectroscopy. The region of frequency of vibration spectra is in the infrared region. The energy change involved due to vibration of molecules is of the order of 10^4 joules / mole.

The vibration of molecule actually gives rise to change in dipole moment. There are three types of molecular vibration.

1. Symmetric stretching vibration.

2. Asymmetric stretching vibration.

3. Bending vibration

Symmetric stretching vibration

When a molecule is alternately stretched and compressed, the dipole moment remains zero during one complete vibration. Such a vibration is called symmetric stretching vibration. As there is no change in dipole moment occurs, this vibration is called infrared inactive.

For example consider the carbondioxide molecule in which the three atoms are arranged linearly. The carbon atom has a positive charge and oxygen atoms have negative charge. During symmetric stretch the molecule is alternately stretched and compressed. (see figure below).
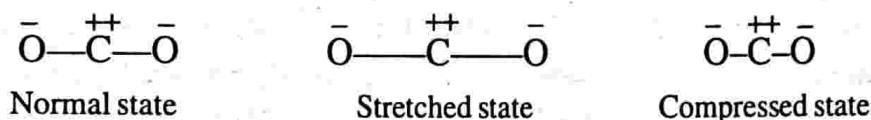
$$\bar{O}-\overset{++}{C}-\bar{O} \qquad \bar{O}-\!\!\!-\overset{++}{C}-\!\!\!-\bar{O} \qquad \bar{O}-\overset{++}{C}-\bar{O}$$

Normal state   Stretched state   Compressed state

Figure 3.3

Asymmetric stretching vibration

When a linear molecule whose one bond stretches while the other bond compresses and vice-versa results in a vibration called asymmetric (Anti symmetric) stretching vibration. During this vibration the dipolement of the molecule changes periodically. Thus the vibration is called infrared active. For example see the asymmetric stretching vibration of carbon dioxide molecule.
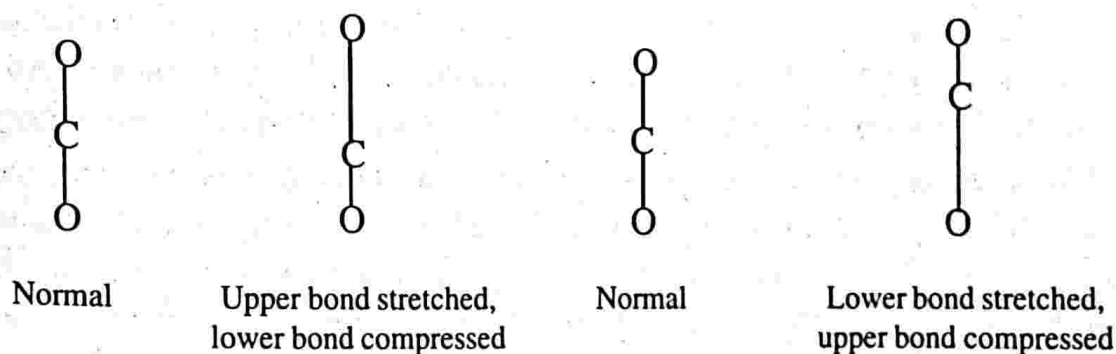
Normal   Upper bond stretched,   Normal   Lower bond stretched,
                 lower bond compressed   upper bond compressed

Figure 3.4

Bending vibration

A linear molecule wholes bonds bend upwards making an angle then come to normal state then bonds bend downward and again come to normal state is called

bending vibration. For such a vibration the dipole moment of the molecule changes periodically and thus infrared active. For example see the figure of bending vibration of carbondioxide molecule.
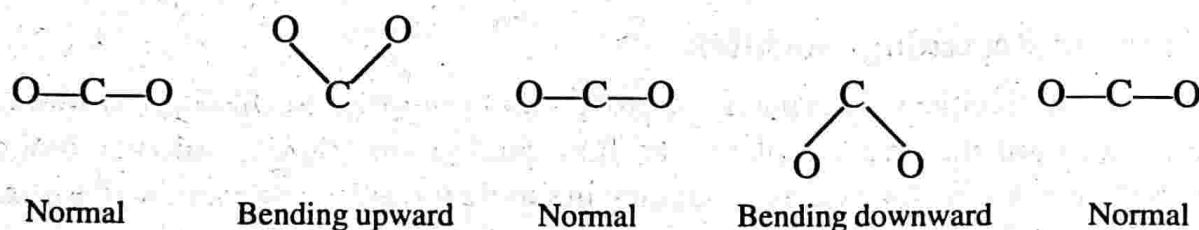

| Normal | Bending upward | Normal | Bending downward | Normal |

Figure 3.5

4. Visible and ultraviolet region

This region extends from 3×10^{14} Hz to 3×10^{16} Hz (1µm to 10nm wavelength).

When the valence electrons of an atom jump from one energy level to another level we get emission or absorption spectrum. It is called electronic spectrum and the study of electronic spectrum is known as electronic spectroscopy. The frequency region of electronic spectra lies in 3×10^{14} Hz to 3×10^{16} Hz. i.e., It lies in the visible and ultraviolet regions. The energy change involved is of the order of 10^5 joules / mole.

5. X-ray region

This region extends from 3×10^{16} Hz to 3×10^{18} Hz (10nm to 100pm wavelength).

When an electron strikes a target, before stopping it makes several collisions with the atoms in the target. It may interact with atoms in two ways.

(i) When an electron interacts with the strong electric field of the atomic nucleus, consequently it is decelerated. According to classical electromagnetic theory, it would radiate electromagnetic energy continuously. This process can be thought as if the electron is emitting a series of photons with varying energy. An energetic electron passing through matter will radiate photons and lose energy.

The process by which photons are emitted by an electron slowing down is called bremsstrahlung (German word for braking radiation). These emitted photons are called X-rays. The X-rays produced in this process are called bremsstrahlung X-rays or continuous X-rays. The frequency of such X-ray lies in the above said region.

(ii) When a high energy electron collides with one of the K-shell electrons in a target atom, enough energy may be transferred, to the K electron, the atom may be ionised. It will be left with a vacancy in its K shell. The atom is most stable in its lower energy state so an electron from one of the higher shells will change its

state and fill the inner shell vacancy at lower energy, emitting radiation. When this occurs in a heavy atom, we call the electromagnetic radiation emitted an X-ray. The photons emitted in such a manner are called characteristic X-rays.

The frequency of such X-rays lies in the above said region.

The energy changes involving the above said processes is of the order of 10^7 joules/ mole. The study of X-ray spectrum is called X-ray spectroscopy.

6. Gramma ray region

This region extends from 3×10^{18} Hz to 3×10^{20} Hz (100 pm to 1 pm wavelength).

It is due to rearrangement of nuclear particles electromagnetic radiations are emitted from a nucleus. These photons are called gamma rays. The energy change involved in this process is 10^9 to 10^{11} joules per atom and frequency range lies in the above said region. The study of the spectrum under this region of frequency is called γ-ray spectroscopy.

Apart from the six spectroscopies discussed, there is one more important spectroscopy called Raman spectroscopy discovered by sir C.V. Raman.

Representation of spectra

In this section we shall deal with how to record a spectrum. For this we use a grating spectrometer (Dispersive spectrometer). Grating spectrometer is suitable for use in the ultraviolet, visible and infrared regions of the spectrum.

Grating spectrometer

It consists of a source of radiation S. Usually a white source is taken as the source since it emits radiation over a wide range of frequencies. The radiation from the source is allowed to pass through a narrow slit S_1 and falls on a concave mirror M_1 from which a parallel beam of light is reflected onto a grating which is fixed on turn table. The grating reflects many frequencies at different angles. This reflected beam is allowed to fall an another concave mirror from which it is focussed to pass through a slit S_2. From S_2 the radiation falls on M_3 by which it is focused on to the detector. Detector is placed at the focus of the mirror M_3. Detector is a thermocouple for infrared radiation or a photomultiplier for visible and ultraviolet radiation. Depending upon the intensity of radiation falling on the detector, the detector gives an electric signal. This signal is amplified electronically and used to drive a pen which records the spectrum. The amplified signal can also be given to computer which can draw the spectrum and can be stored in it for future processing.
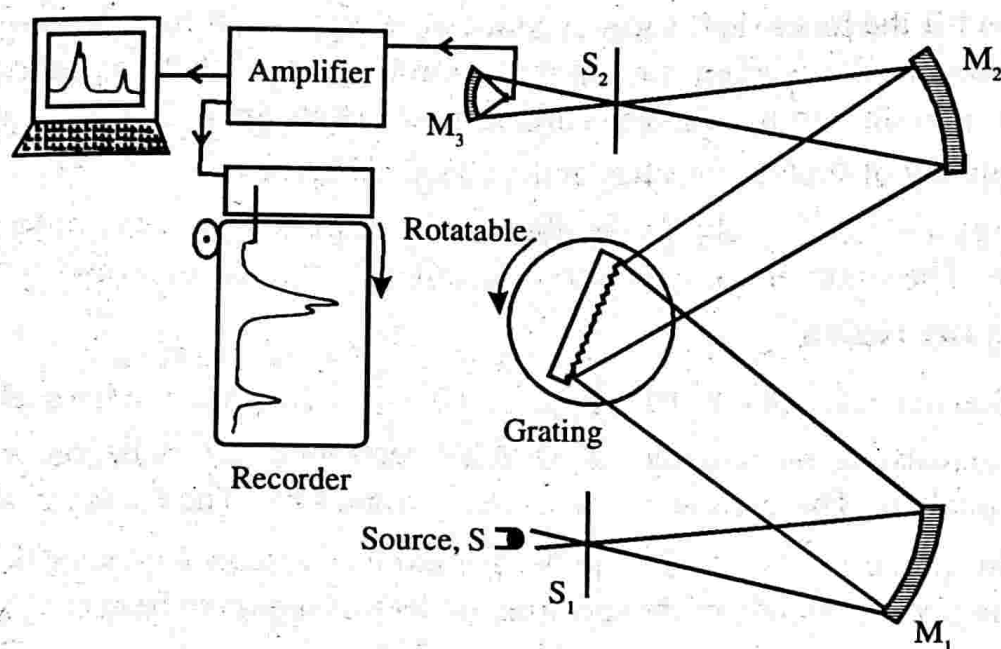
Figure 3.6: Grating spectometer

Purpose of slits

1. Slits provide a sharply defined image which can be focussed on the detector.

2. Since the slits are made narrow, the frequency range of radiation which passes through the slits are smaller, consequently the resolving power of the instrument is increased.

3. Narrow slits prevent stray radiations coming from various components of spectrometer owing to scattering stray radiations entering the detector can make the recording false. This can be avoided to an extend using narrow slits.

Recording a spectrum

There are mainly two ways of recording a spectrum. One is the frequency domain spectrum, the other is the time domain spectrum. In the frequency domain spectrum we record the detector output against frequency. In the time domain spectrum we record the detector output against time. Here we shall discuss only frequency domain spectrum.

Now let us consider how a spectrum is recorded. If there is no sample present, detector output will be a constant over the range of frequencies covered by the instrument. This is only an ideal case. Now we shall see how to plot this on a chart paper. In frequency spectrum usually we plot percentage of frequency on the horizontal axis with increasing frequency and percentage detector output on the left vertical axis with 100% detector output as the origin and 0% at the top of the axis.

On the extreme right vertical axis we simultaneously mark the energy absorbed by the sample with zero energy absorbed as the starting point (at the bottom) and 100% energy absorbed at the top. When there is no sample the detector output will be 100% and will be a constant over the range of frequencies and the energy absorbed is zero. The corresponding frequency spectrum is shown in graph given below.
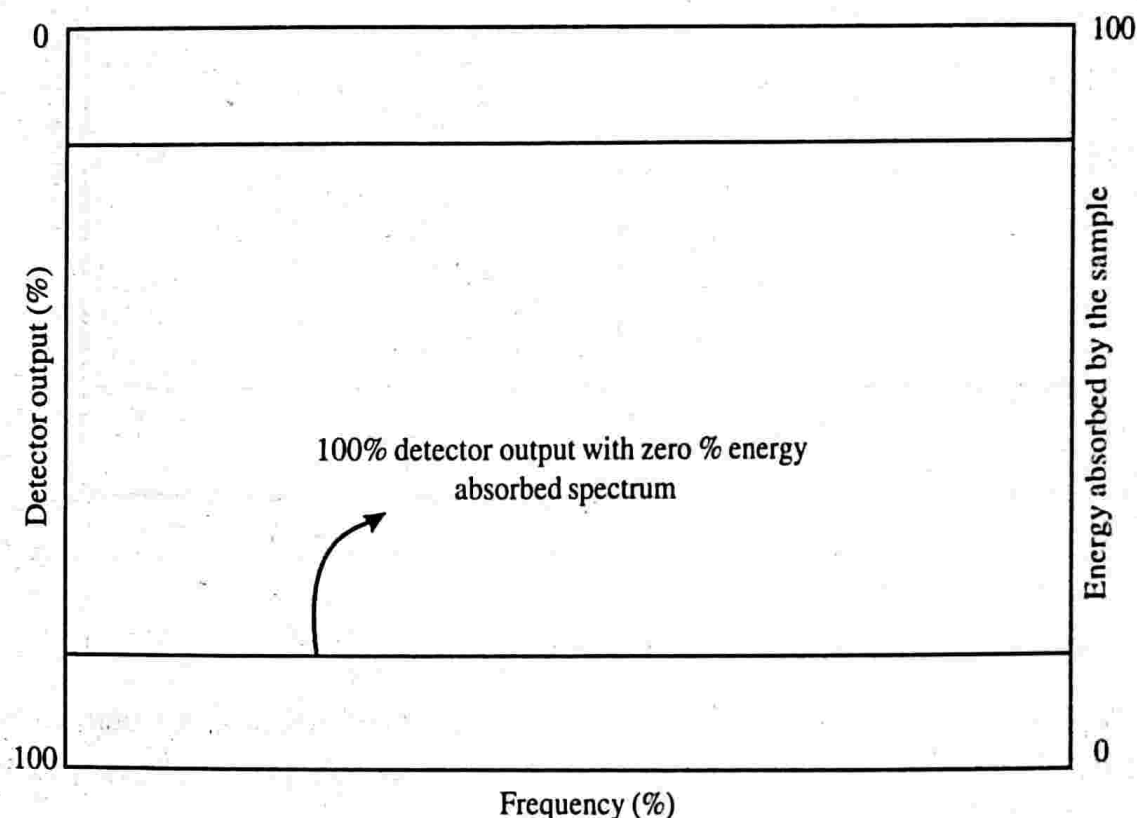

0   100

Detector output (%)   Energy absorbed by the sample

100% detector output with zero % energy
absorbed spectrum

100   0

Frequency (%)

Figure 3.7

Now we imagine a substance placed in the path of the beam. The substance can be placed anywhere in the path of the beam. In order to minimise the size of the substance it is placed close to one of the slits S_1 or S_2 where the beam is narrow. Usually the substance is placed near the slit S_2 where the frequency range is small which is admitted by the grating. Suppose that our substance is having only two possible energy levels E_1 and E_2. The frequency corresponding to these levels is

given by $v = \dfrac{E_2 - E_1}{h}$. Thus some energy at this frequency will be absorbed by the

substance (sample) from the radiation falling on it. As a result the detector output will show a sudden fall at this frequency. The corresponding frequency spectrum is shown in figure below.
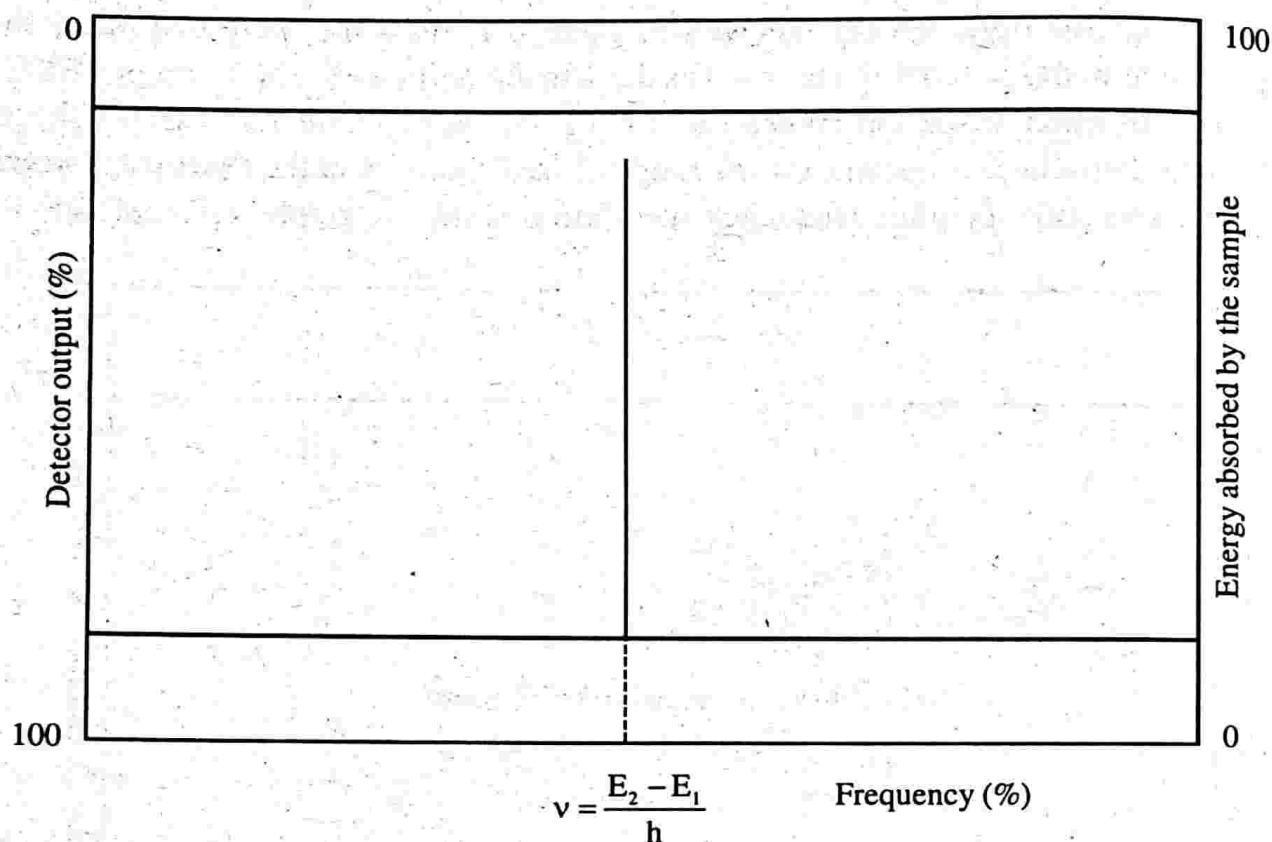
$$\nu = \frac{E_2 - E_1}{h}$$

Frequency (%)

Figure 3.8

The above discussion of frequency spectrum is ideal and will not be obtained in practice. In actual practice so many other factors will come into play so the spectrum obtained will be different from that we already explained.

Factors affecting ideal spectrum

While drawing ideal spectrum we didn't say anything about the source emissivity and sensitivity of the detector. Actually both of them are frequency dependent. Because of this the horizontal line obtained in the case of no sample conditions will be no longer horizontal. Moreover the detector, the amplifier, the pen recorder etc. can disrupt the horizontal line and provide with larger number of extraneous frequencies arising from randomly generated electrical signals.

In ideal frequency spectrum we obtained a single frequency line spectrum. In actual practice this is not so. This is because a range of frequencies are falling on the detector rather than a single frequency since it is impossible to make the slit infinitesimally narrow. Apart from this the energy transitions in atoms or molecules donot occur at a single frequency but always occur over a range of frequencies. As a result the spectral absorption frequency line will be broadened. The actual frequency spec-

trum is shown in figure below. It may be noted that in this transmittance is plotted as the detector output and absorbance as the energy absorbed.
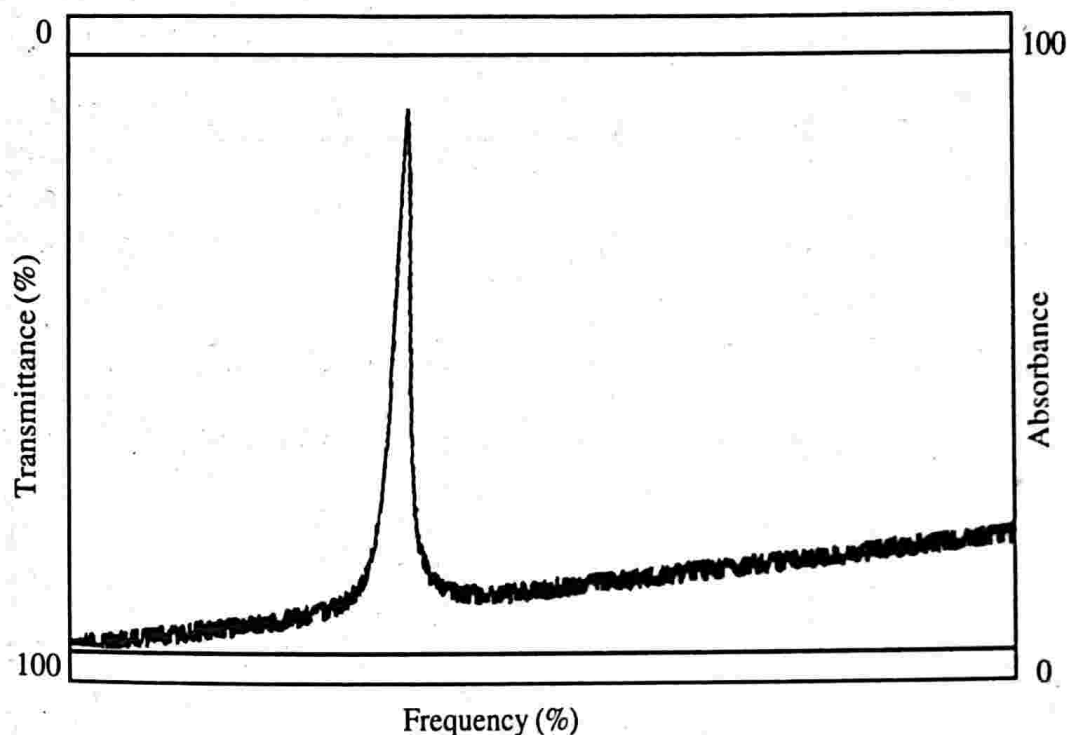

Figure 3.9

Note : - Transmittance $T_\lambda = \dfrac{I}{I_o}$, where I_o is the intensity of incident radiation and I

is the intensity of radiation transmitted out of the sample. Whatever be the frequency range in which the spectrometer operate most of the modern spectrometers trace out the frequency spectrum as discussed above. However there is another very effective plotting method is followed, which is called the derivative of spectral trace. Here the derivative of energy absorbed or emitted is plotted against frequency. This has mainly two advantages over the former one. One is that from the absorbance trace we can exactly locate the centre of a absorbance peak. Because at this point the curve of absorbance (A) is horizontal hence it slope $\left(\dfrac{dA}{dv}\right)$ is zero. Secondly the half width

of the absorbance peak can be easily found out from the derivative curve see figure below. This type of tracing curve is adopted in electron paramagnetic resonance spectrometer.
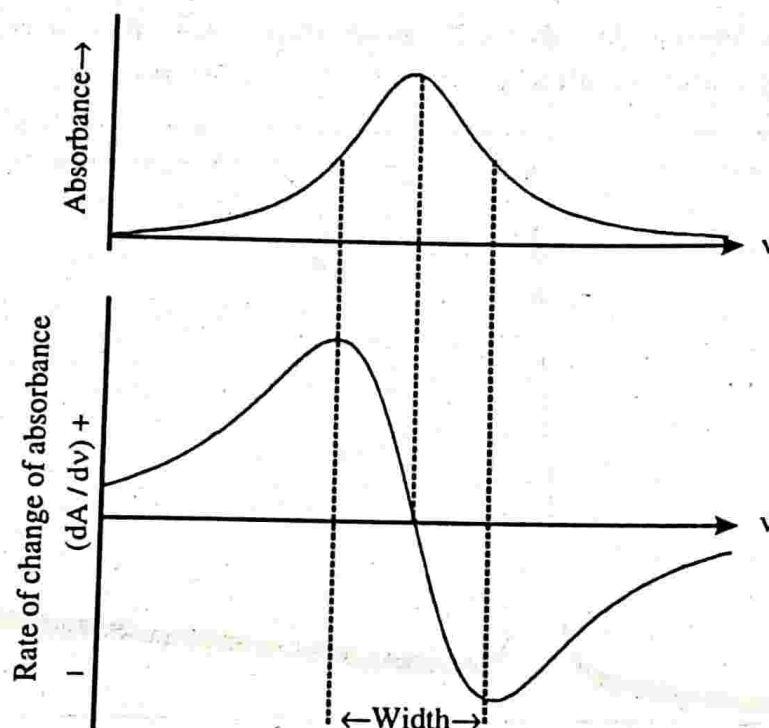
Figure 3.10

Basic elements of practical spectroscopy

Spectrometers play a vital role in the field of practical spectroscopy. Spectrometers used in various regions of spectrum differ widely from each other in construction. Here we shall discuss about the absorption and emission spectrometers whose basic features are common to all types of spectrometers.

Absorption spectrometer

It is of two types one used in the infrared, visible and ultraviolet regions and the other one used in the microwave and radio frequency regions. It consists of a radiation from a white source from which radiation is allowed to fall on a sample. The radiation coming out of the simple passes through an analyser (grating) which selects the frequency reaching the detector. The signal from the detector passes to a recorder which is synchronized with the analyser so as to produce a trace of the absorbance as the frequency varies. In between the sample and the analyser a modulator is placed. The modulator is an electronic device (or mechanical) which interrupts the radiation beam a certain number of times per second, usually between 10 and 1000 times. This is to cause the detector to send an alternating current signal to the recorder with a fixed frequency of 10-1000Hz. It has two advantages. One is the amplifier in the recorder is of a-c type which is in general simpler to construct and

more reliable in operation than a d. c. amplifier. The amplifier can be tuned to select only that frequency which the modulator imposes on the signals thus ignoring all other signals. In this way stray radiation and other extraneous signals are removed from the spectral trace.

In the microwave and radio frequency regions it is possible to construct mono-chromatic sources whose emission frequency can be varied over a range. In this case no separate analyser is required since source acts as its own analyser. As there is no analyser it is necessary for the recorder to be synchronised with the source - scanning device in order that a spectral trace be obtained.
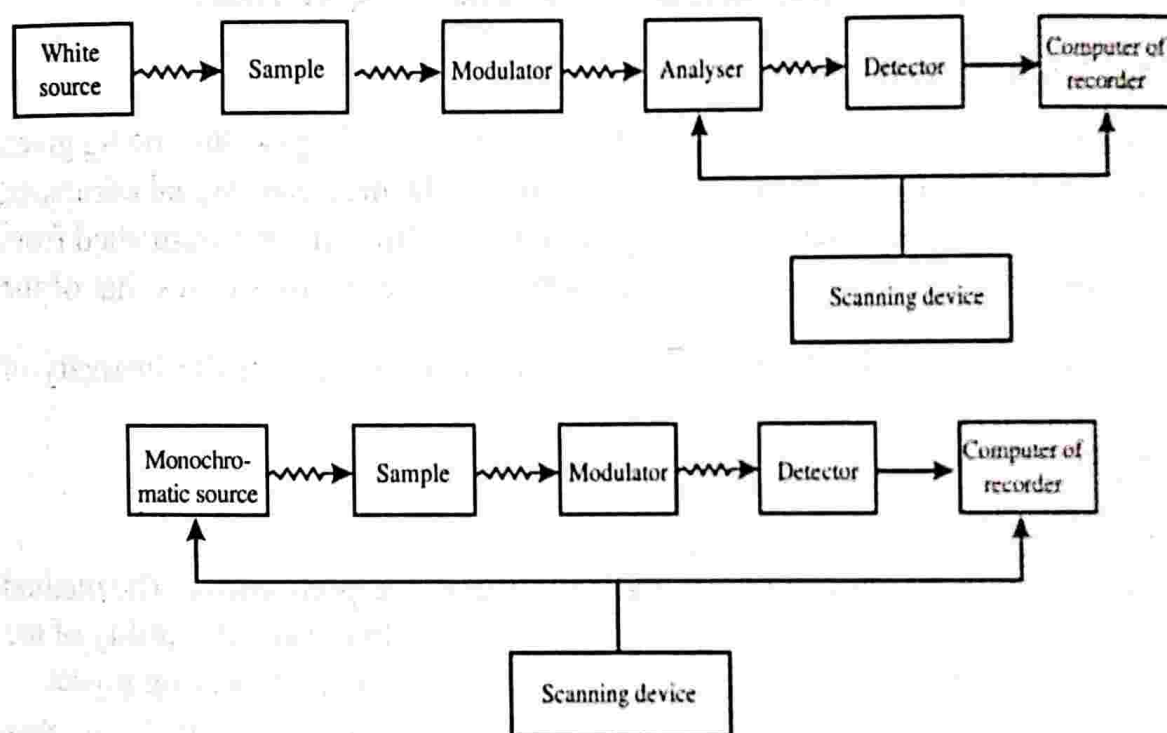

Figure 3.11

Emission spectrometer

It consists of a source of excitation, modulator, analyser, detector and a recorder placed as shown in figure. A sample is placed in between the modulator and the analyser. The analyser and the recorder are connected to a scanning device.

The excitation can be thermal or electrical but takes the form of electromagnetic radiation. The modulator is placed between the source of excitation and the sample, together with a tuned detector - amplifier, ensures that the only emission recorded from the sample arises directly from excitation. i.e., any other spontaneous emission is ignored.
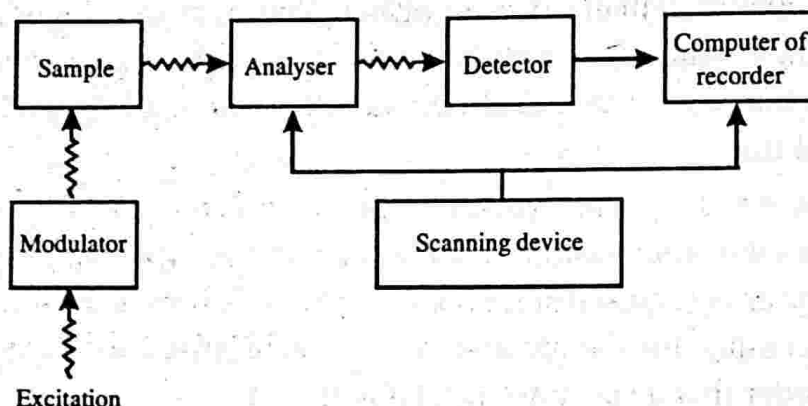
Figure 3.12: Block diagram of a typical emission spectrometer

Signal to noise ratio (S/N)

Signal to noise ratio is the signal divided by the noise, both quantities being given in the same units. It gives the relative importance of the measured signal compared to the noise in the measurement. The signal must be sufficiently distinguished from the noise, for this the intensity of the signal must be three or four times that of the noise. i.e., $\dfrac{S}{N} = 3$ or 4. This requirement places a lower limit on the intensity of observable signal.

Resolving power

Resolving power actually measures the performance of a spectrometer. The method of separating two near by frequency spectra is called resolution and the ability of the spectrometer to produce separate frequency spectra is called its resolving power.

The resolving power actually depends upon the exit slit width. We know that molecular absorption takes place over a spread of frequencies. Usually this is very narrow. Let us consider two such frequency spectra lying close to each other. These spectra overlap in some region and become a single frequency spread as shown in figure. Suppose this spectra is allowed to pass through the exit slit of width larger than the frequency line width. In this situation both peaks of the spectra steadily passes through the slit and reaches the detector. Thus we can say that spectra is not resolved. If we decrease the slit width so that it allows only one peak to pass through. This shows that a narrower slit width would result in their resolution. This happens when the slit width is less than the separation between the frequency lines. But the narrow slit (high resolving power) brings a problem. A narrower slit allows only less energy to pass through. As a result the strength of the signal reaching the detector would be weak. Thus it is not possible to distinguish the signal from the noise. So we have to make a compromise between the resolving power and signal to noise

ratio. Thus in experimental spectroscopy we have to find the minimum slit width (maximum resolving power possible) consistent with acceptable signal to noise values.

Note :   It may be noted that the above discussion about resolving power is not precise.
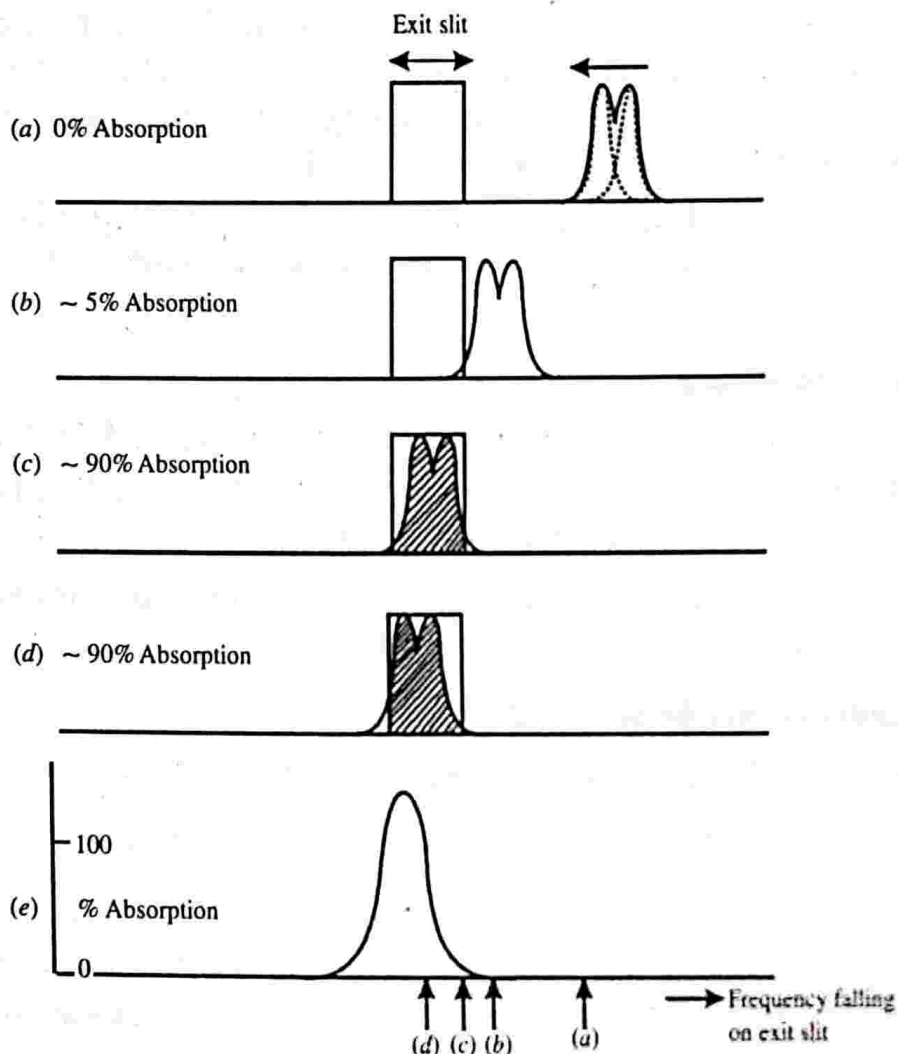

Figure 3.13: Illustrating the relationship between slit width and resolving power

The width and intensity of spectral transitions

The width and intensity are two properties of spectral transitions.

The width of spectral lines

We have seen that absorptions and emissions take place not at a single frequency but varied over a range. Thus the spectral lines obtained will be broadened and we have found that how the width of a spectral line is measured. The width of spectral lines arise because the energy levels of atomic and molecular systems are not precise. This occurs due to several factors such as collision broadening, Doppler broadening, Heisenberg uncertainty principle etc.

Collision broadening

Atoms and molecules in liquids and gases are in continual motion and collide frequently with each other. These collisions cause some deformations in the energy levels of outer most electrons. It is due to this visible and ultraviolet spectral lines have widths. It may be recalled that in visible and ultraviolet regions transitions occur in outer electronic shells. The collisions can also affect the vibrational and rotational spectra which explains the width of these spectral lines. When molecular interactions are strong we get more broadening. This is why spectra of gases are more sharp than those of the corresponding liquids.

In the case of solids interactions are less, thus we get sharp spectra. But solid spectral lines split into two or more components showing the evidence of interaction.

Doppler broadening

It is due to Doppler effect the particles show a Doppler shift (change in frequency). Since the motion is random the shift occurs in both lower and higher frequency regions. This results in the broadening of spectral lines.

In general, collision broadening is dominant in liquids where as Doppler broadening dominates in gases.

Uncertainty principle broadening

According to Heisenbergs energy-time uncertainty, we have

$$\Delta E \, \Delta t \approx \frac{h}{2\pi}$$

where ΔE is the energy uncertainty of a state in which the system stays for Δt second. h is the Plancks constant. If the system is in the ground state for an infinite time ($\Delta t = \infty$) then $\Delta E = 0$. i.e., energy uncertainty is zero. In otherwords ground state energy is sharply defined. However, the life time (Δt) of an excited electronic state is about 10^{-8} s.

$$\therefore \qquad \Delta E = \frac{h}{2\pi \Delta t} = \frac{6.62 \times 10^{-34}}{6.28 \times 10^{-8}} \approx 10^{-24}$$

∴ The corresponding uncertainty associated with frequency is

$$\Delta \upsilon = \frac{\Delta E}{h} = \frac{10^{-24}}{6.6 \times 10^{-34}} \approx 10^{8} \, Hz$$

This is actually a large uncertainty. But this is small compared to the radiation

frequency of such transitions $10^{14} - 10^{16}$ Hz. So the natural line width is said to be small. But in the case of electron spin state $\Delta t \approx 10^{-7}$ s

$\therefore \qquad \Delta \upsilon \simeq 10^7$ Hz

This frequency is very large when compared with the usual frequency of such transitions, $10^8 - 10^9$ Hz. Thus spectral lines becomes broader. In this context broadening due to uncertainty principle becomes an important factor. In electronic transitions collision and Doppler broadening are more important.

The intensity of spectral lines

A spectral line is an isolated dark or bright line resulting from a deficiency or excess of photons in a narrow frequency range compared with nearby frequencies.

Intensity actually means the radiant flux passing through unit area in unit time.

In spectroscopy we usually measure the relative intensities of spectral lines. The intensity of spectral lines depends on

(i) The transition probability between the two states (selection rules)

(ii) Population of states $\dfrac{N_2}{N_1} = e^{-\frac{\Delta E}{kT}}$

(iii) In absorption sample path length l and concentration c.

The relationship between concentration c, path length l and the incident (I_o) and transmitted intensities of radiation is written as

$$\frac{I}{I_o} = e^{-kcl} \qquad\qquad ..... (1)$$

where k is a constant for the particular spectroscopic transition under investigation. The above equation can also be written in another form with base 10 instead of base e using base changing rule for convenience.

Taking log on both sides we get

$$\ln\left(\frac{I}{I_o}\right) = -kcl$$

$$\ln_e\left(\frac{I}{I_o}\right) = \ln_{10}(I/I_o)\ln_e 10$$

But $\ln_e 10 = 2.303$

$$\therefore \quad 2.303 \ln_{10}(I/I_0) = -kcl$$

or

$$\ln_{10}\left(\frac{I}{I_o}\right) = -\frac{k}{2.303}cl = -\varepsilon cl$$

or

$$\frac{I}{I_o} = 10^{-\varepsilon cl} \qquad\qquad\qquad ..... (2)$$

The ratio $\dfrac{I}{I_o}$ is called the transmittance and is denoted by T.

$$\therefore \quad T = 10^{-\varepsilon cl}$$

Here ε is called the molar absorption coefficient or decadic extinction coefficient. or decadic absorptivity (decadic meaning related to base 10).

From equation 2, we get

$$\log\left(\frac{I}{I_o}\right) = -\varepsilon cl$$

or

$$\log\left(\frac{I_0}{I}\right) = \varepsilon cl = A$$

where A is called the absorbance or optical density.

The equation $A = \varepsilon cl$ is called Beer-Lambert law.

Since absorbance of a sample is proportional to l and c of the absorbing species absorbance measurements are carried out in spectrometers rather than transmittance $\left(\dfrac{I}{I_0}\right)$ which depends on l and c exponentially.

IMPORTANT FORMULAE

1. Energy quantisation: $E_2 - E_1 = h\nu$

2. Expression for transmittance:

$$T_\lambda = \frac{I}{I_0}$$

I_0 is the intensity of the incident radiation and I is the intensity radiation transmitted out.

3. Uncertainty principle:

$$\Delta E \Delta t = \frac{h}{2\pi}$$

$$\Delta E = h\Delta\nu$$

or

$$\Delta\nu = \frac{\Delta E}{h} \approx \frac{1}{2\pi\Delta t}$$

4. Intensity of spectral lines:

   (i) Population of states, $N_2 = N_1 e^{-\frac{\Delta E}{kT}}$

   (ii) The relation between concentration C, path length l, the incident intensity (I_0) and the transmitted intensity (I) radiation

$$\frac{I}{I_0} = e^{-kcl}$$

or

$$\frac{I}{I_0} = 10^{-\epsilon cl}, \quad \epsilon = \frac{k}{2.303}$$

$$\frac{I}{I_0} = T \quad \text{Transmittance}$$

$$T = 10^{-\epsilon cl}$$

5. Beer-Lambert law: $A = \epsilon cl$

UNIVERSITY MODEL QUESTIONS

Section A

(Answer questions in two or three sentences)

Short answer type questions

1. What is spectroscopy?

2. What is meant by quantization of energy?
3. Which are the three types of energies possessed by a molecule?
4. Classify spectroscopy in accordance with electromagnetic spectrum.
5. Why a polar molecule is said to be microwave active?
6. What is meant by microwave inactive molecules?
7. Which are the three types of molecular vibrations?
8. What are the factors affecting ideal spectrum?
9. Give the block diagram of absorption spectrometer.
10. Draw the block diagram of emission spectrometer.
11. Define signal to noise ratio. What is its physical significance?
12. What are the properties of spectral line transitions?
13. What are the factors on which the intensity of spectral line depend.
14. Define (i) transmittance (ii) absorbance.
15. What is the relation between transmittance and absorbance?
16. What are the factors on which absorbance of a sample depend?
17. Write down the Beer-Lambert law and explain the symbols.

Section B
*(Answer questions in a **paragraph** of about half a page to one page)*

Paragraph / Problem type questions

1. Briefly explain N.M.R.
2. Briefly explain E.S.R.
3. Explain briefly the symmetric stretching vibration of a molecule.
4. Explain the asymmetric stretching vibration of a molecule.
5. Explain the bending vibration of a molecule.
6. Explain how collision of atoms or molecules in liquids and gases leads to broadening of spectral lines.
7. Explain the Doppler broadening of spectral lines.
8. Explain the broadening of spectral lines due to uncertainty principle.
9. How does the widening of the slits in a spectrometer affect its resolution?

Section C
*(Answer questions in about **two** pages)*

Long answer type questions (Essays)

1. What is a grating spectrometer? Explain the recording of a spectrum with diagram.